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We study the adsorption of flexible polymer macromolecules on a percolation cluster, formed by a regular two-dimensional disordered lattice at critical concentration p_c of attractive sites. The percolation cluster is characterized by a fractal dimension $d_s^{p_c} = 91/49$. The conformational properties of polymer chains grafted to such a fractal substrate are studied by means of the pruned-enriched Rosenbluth method. We find estimates for the surface crossover exponent governing the scaling of the adsorption energy in the vicinity of transition point, $\phi_s^{p_c} = 0.425 \pm 0.009$, and for adsorption transition temperature, $T_A^{p_c} = 2.64 \pm 0.02$. As expected, the adsorption is diminished when the fractal dimension of the substrate is smaller than that of a plain Euclidean surface. The universal size and shape characteristics of a typical spatial conformation which attains a polymer chain in the adsorbed state are analyzed as well. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.3691102]

I. INTRODUCTION

The conformational properties of polymer macro-molecules in the vicinity of substrates are the subject of continuous interest in polymer science, playing an important role both in technology (adhesion, stabilization of colloidal dispersions[1]) and biological physics (proteins adsorption on membranes[2,3]). The presence of an energetically neutral surface produces only trivial effects of steric restrictions for polymers. More interesting is the case of an attractive substrate, when below a critical temperature T_A, a second-order phase transition into an adsorbed state takes place.[4] The peculiarities of adsorption of grafted polymers on attractive surfaces are thoroughly studied by now both analytically[5–9] and numerically.[6,10–15] As an order parameter of the adsorption transition, one considers the fraction of the average number of monomers N_s adsorbed to the surface and the total length N of the polymer chain, which tends to zero in the usual bulk regime and becomes macroscopic close to T_A, obeying the scaling law

$$\frac{\langle N_s \rangle}{N} \sim N^{\phi_s - 1}, \quad N \to \infty. \tag{1}$$

Here, ϕ_s is the surface crossover exponent, a basic parameter in scaling analysis of the adsorption transition ($0 < \phi_s < 1$). Recent estimates of the crossover exponent ϕ_s along with numerical values for the adsorption temperature T_A are given in Table I.

The study of polymers near disordered surfaces is of great importance, since most naturally occurring substrates are rough and energetically (or structurally) inhomogeneous. Surface heterogeneity has a crucial effect on polymer adsorption phenomena.[16–24] In fact, already simple physical arguments lead to the conclusion that upon increasing the

surface irregularity the number of polymer-surface contacts is strongly influenced, leading to a shift of the adsorption critical temperature. Energetical inhomogeneity arises due to the presence of various chemical compounds in the substrate, interacting with the monomers of the polymer chain in a different manner. In the language of lattice models, such surfaces can be modeled as a two-dimensional regular lattice with different types of randomly distributed sites, e.g., one type with attractive interactions with the monomers and the other one being neutral (treated as defects or impurities). Similarly as it holds in the bulk case,[25,26] presence of uncorrelated point-like defects of low concentration (well below the percolation threshold $p_c = 0.592746$ (Ref. 27)) is expected to be irrelevant for the scaling properties of the adsorption transition of polymers. Numerical simulations[21,24] reveal, however, a continuous dependence of the transition temperature T_A on the concentration p of attractive sites. In particular, close to p_c, the estimate $T_A^{p_c} \simeq 2.3$ was obtained. The related problem of the impact of long-ranged correlations in the distribution of defects on the surface, leading to a non-trivial influence on scaling near the adsorption transition point, was studied recently in Ref. 23.

Since most chemical substrates are proved to be of fractal nature,[28] studying the influence of a non-trivial surface geometry on polymer adsorption is of particular interest. In Ref. 29 it was found that the crossover exponent ϕ_s for a substrate characterized by the fractal dimension d_s^f has upper and lower bounds given as

$$1 - \left(3 - d_s^f\right)\nu \le \phi_s \le d_s^f/3, \tag{2}$$

where ν is the bulk radius of gyration exponent for a polymer chain in a good solvent ($\nu = 0.5887 \pm 0.0006$ (Ref. 30)). One can thus conclude that adsorption is enhanced (diminished) when the fractal dimension of the substrate is larger (smaller) than that of a plain Euclidean surface. A number of studies has been dedicated to polymer adsorption on a family of finitely ramified fractals.[31–34] Also of great importance is the study

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TABLE I. Crossover exponent ϕ_s and adsorption critical temperature T_A for polymers grafted on a homogeneously attractive plain surface and on the fractal surface formed by a percolation cluster (ϕ_s^{pc}, T_A^{pc}). RG: renormalization group studies, MC: Monte Carlo simulations.

	ϕ_s	T_A	ϕ_s^{pc}	T_A^{pc}
RG	0.482[5]			
	0.518[8]			
MC	0.496 ± 0.005[11]	3.497 ± 0.003[11]	0.425 ± 0.009	2.64 ± 0.02
			(this study)	(this study)
	0.484 ± 0.002[13]	3.5006 ± 0.0009[13]		

of polymers in the vicinity of fluctuating surfaces, such as membranes.[35,36]

In this concern, it is worthwhile to study the situation when the concentration of attractive sites on the surface is exactly at the percolation threshold and a spanning percolation cluster of attractive sites appears. A percolation cluster is a fractal object with fractal dimension $d_s^{pc} = 91/49 \simeq 1.89$.[37] In general, studying polymer adsorption on a percolative surface, one encounters two possible statistical averages. In the first (considered previously in Refs. 21 and 24), the statistical ensemble includes all attractive sites on the surface, whereas in the second, one takes into account only sites belonging to the percolation cluster. In the present study, we consider the particular situation, when the neutral sites of the surface (which do not belong to the percolation cluster) are penetrable for the polymer chain, and the polymer is adsorbed on the attractive fractal with fractal dimension d_s^{pc}. This can model the process of polymer adsorption on an attractive, partially penetrable "sieve" (see Fig. 1), which could be of interest in biophysical applications.

II. THE METHOD

We start with a regular two-dimensional lattice of edge lengths up to $L_{max} = 400$, each site of which is assigned to be occupied with percolation probability p_c and empty otherwise. To extract the percolation cluster of occupied sites, which spans around the lattice, an algorithm based on the site-labeling method of Hoshen and Kopelman[38] has been applied.
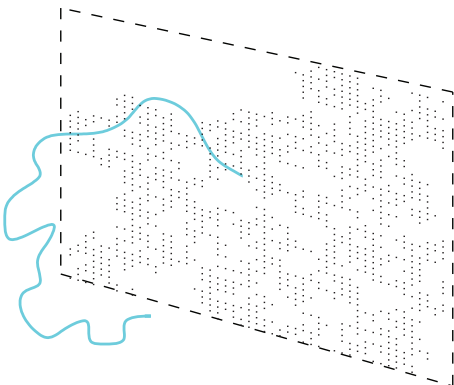

FIG. 1. Sketch of a polymer chain grafted to an attractive "sieve" formed by a percolation cluster.

Note, that the definition of spanning clusters on finite lattices is not unique, in particular one could consider clusters connecting only two opposite borders. In this case, however, the constructed clusters are anisotropic in space and could be related to the problem of so-called directed percolation.[39] We therefore take only incipient clusters into account which reach the borders of the lattice in *all* coordinate directions and hence are expected to be more isotropic.

The polymer chain is modeled as a self-avoiding walk (SAW). To study the conformational properties of SAWs, grafted to the substrate formed by a percolation cluster, we apply the pruned-enriched Rosenbluth method (PERM).[40] The starting point of a SAW is fixed on a random site which belongs to the percolation cluster (see Fig. 1). Note, that this starting site is always chosen within a small region around the center of a given percolation cluster to allow the adsorbed polymer chain configurations to be completely located on the cluster. We treat this disordered surface as $z = 0$ plane of a regular three-dimensional lattice. The chain grows step by step, i.e., the nth monomer is placed at a randomly chosen neighbor site of the last placed $(n − 1)$th monomer ($n \leq N$), taking into account that the chain cannot "penetrate" through the occupied sites of the surface (belonging to the percolation cluster), but only through the empty sites. The growth is stopped, if the total length of the chain, N, is reached (we consider SAWs of length up to $N = 150$). The adsorption energy E_n of a growing chain at the nth step is given by

$$E_n = N_s(n)\,\varepsilon, \quad (3)$$

where ε is the attractive energy between monomers and the percolation cluster sites, and $N_s(n)$ is the number of contacts of the polymer chain with attractive sites.

A weight W_n is given to each sample configuration at the nth step, which in our case is given by

$$W_n = \prod_{l=2}^{n} m_l \mathrm{e}^{-\frac{E_l - E_{l-1}}{k_B T}}. \quad (4)$$

Here, m_l is the number of free lattice sites to place the lth monomer and k_B is the Boltzmann constant. In what follows, we will assume units in which $\varepsilon = −1$, $k_B = 1$. Pruning and enrichment are performed by choosing thresholds $W_n^<$ and $W_n^>$ depending on the current estimate of the sum of weights $Z_n = \sum_{\mathrm{conf}} W_n^{\mathrm{conf}}$ of the n-monomer chain.[40–42] If the current weight W_n of an n-monomer chain is less than $W_n^<$, the chain is discarded with probability 1/2, whereas if W_n exceeds $W_n^>$, the configuration is doubled (enrichment of the sample with high-weight configurations).

The configurational averaging for any observable O is given by

$$\langle O \rangle = \frac{\sum_{\mathrm{conf}} W_N^{\mathrm{conf}} O}{\sum_{\mathrm{conf}} W_N^{\mathrm{conf}}}, \quad (5)$$

where W_N^{conf} is the weight of an N-monomer chain in a given configuration. In the problem under consideration, a double averaging has to be performed: The first $\langle \ldots \rangle$ over all configurations of the polymer chain grafted to a single percolation cluster; the second average $\overline{\langle \ldots \rangle}$ is carried out over different realizations of disorder, i.e., over different constructed
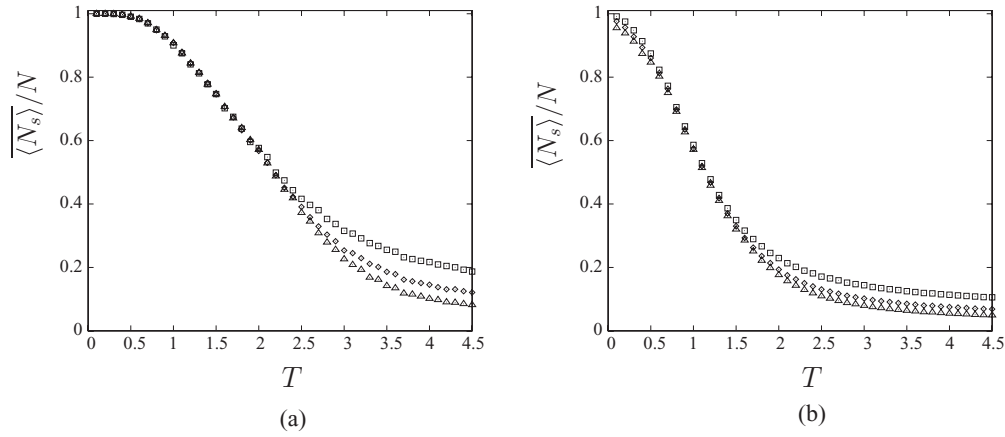
FIG. 2. Averaged fraction of monomers of the chain adsorbed on (a) a homogeneously attractive surface and (b) an attractive percolation cluster for $N = 40$ (squares), $N = 80$ (diamonds), $N = 140$ (triangles) as a function of temperature.

percolation clusters

$$\overline{\langle O \rangle} = \frac{1}{M} \sum_{i=1}^{M} \langle O \rangle_i. \tag{6}$$

Here, M is the number of different clusters and the index i means that a given quantity is calculated on cluster i. We constructed $M = 1000$ clusters. Note, that the case of so-called "quenched disorder" is considered, where the average over different disorder realizations is taken after the configurational average has been performed.

III. RESULTS

The adsorption transition is in general viewed as a second-order phase transition[4] with the averaged fraction of monomers on the surface $\langle N_s \rangle/N$ viewed as order parameter. Note that this value can also be interpreted as an adsorption energy per monomer (cf. Eq. (3)). In the thermodynamic limit $N \rightarrow \infty$, the adsorption energy tends to zero in the desorbed phase for $T > T_A$ and becomes macroscopic close to the transition point, where it scales according to Eq. (1):[6]

$$\langle N_s \rangle/N \sim \begin{cases} \frac{1}{(T-T_A)N}, & T > T_A, \\ N^{\phi_s - 1}, & T = T_A, \\ (T_A - T)^{\frac{1-\phi_s}{\phi_s}}, & T < T_A. \end{cases} \tag{7}$$

In the adsorbed phase for $T < T_A$, the fraction $\langle N_s \rangle/N$ is independent of N. Introducing the scaling variable $x = |T - T_A|N^{\phi_s}$, the adsorption energy per monomer can be presented in general in the scaling form

$$\langle N_s \rangle/N = N^{\phi_s - 1} F(|T - T_A|N^{\phi_s}) \tag{8}$$

with

$$F(x) \sim \begin{cases} \frac{1}{x}, & T > T_A, \\ \text{const}, & T = T_A, \\ x^{\frac{1-\phi_s}{\phi_s}}, & T < T_A. \end{cases} \tag{9}$$

Our analysis of the temperature behavior of the order parameter $\overline{\langle N_s \rangle}/N$ for chain lengths up to $N = 140$ is shown

in Fig. 2 (for comparison and to check the validity of our computer code, we re-consider the case of a homogeneous attractive surface as well). The number of contacts with attractive sites of the surface increases monotonically as the temperature is lowered and becomes macroscopic within a short temperature interval close to the adsorption transition. Whereas for the case of a homogeneously attractive surface $\overline{\langle N_s \rangle}/N$ reaches its maximum value close to 1 at $T \ll T_A$ as expected (the polymer lies on $z = 0$ plane), in the case of a fractal surface this value is found to be slightly smaller. Due to the complicated structure of a percolation cluster (in particular the existence of numerous "dead-ends") even at very low temperatures some small percentage of monomers occupy sites of $z = 0$ plane which do not belong to the cluster (as we checked explicitly for idealized clusters constructed by hand) and according to our definition (3) are *not* counted as "adsorbing"; the ground state with lowest energy is thus not reached. This is a dynamic problem which is also encountered in other disordered systems, e.g., in spin glasses. It requires a very long observation time for a polymer to find a configuration completely located on the edges of the percolation cluster.

Due to the presence of the surface, which breaks the space isotropy, one distinguishes between the polymer size characteristics in directions parallel and perpendicular to the surface. Let $\vec{R}_n = \{x_n, y_n, z_n\}$ be the position vector of the nth monomer of the polymer chain ($n = 1, \ldots, N$). The components of squared radius of gyration in direction parallel and perpendicular to the surface are given by

$$R_{g\parallel}^2 = \frac{1}{2N^2} \sum_{n=1}^{N} \sum_{m=1}^{N} [(x_n - x_m)^2 + (y_n - y_m)^2],$$

$$R_{g\perp}^2 = \frac{1}{2N^2} \sum_{n=1}^{N} \sum_{m=1}^{N} (z_n - z_m)^2. \tag{10}$$

The component of the gyration radius in direction perpendicular to the surface (z-direction), $\langle R_{g\perp}^2 \rangle$, can be interpreted as the average thickness of the layer of adsorbed monomers. Well above the transition temperature, it obeys the usual bulk scaling behavior and becomes N-independent in
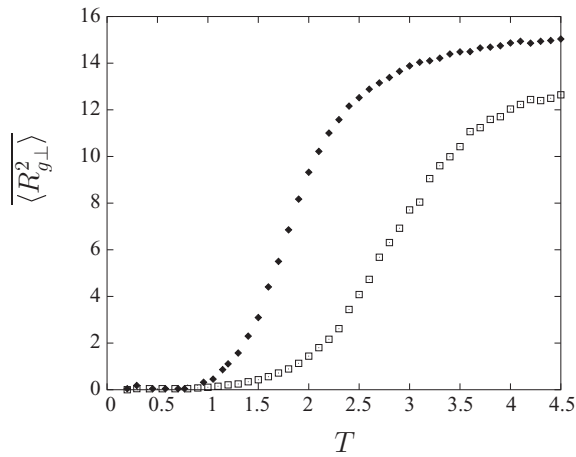
FIG. 3. Component of gyration radius of the polymer chain in direction perpendicular to the surface for the cases of a homogeneously attractive surface (squares) and an attractive percolation cluster (filled diamonds) for $N = 140$ as a function of temperature.

the adsorbed phase[6]

$$\langle R_{g\perp}^2 \rangle \sim \begin{cases} N^{2\nu}, & T > T_A, \\ (T_A - T)^{-\frac{2\nu}{\phi_s}}, & T < T_A. \end{cases} \quad (11)$$
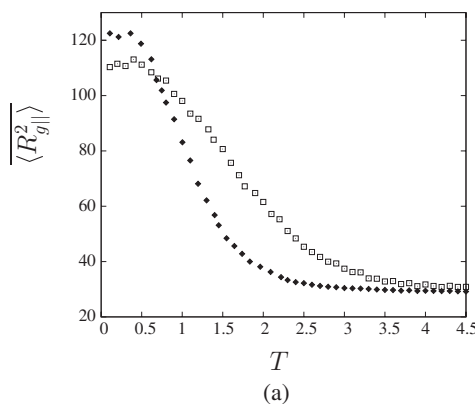
Here, ν is a well-known universal critical exponent, governing the scaling of the radius of gyration in the bulk ($\nu = 0.5887 \pm 0.0006$ (Ref. [30])). The corresponding scaling ansatz is then

$$\langle R_{g\perp}^2 \rangle \sim N^{2\nu} G_\perp(|T - T_A|N^{\phi_s}), \quad (12)$$
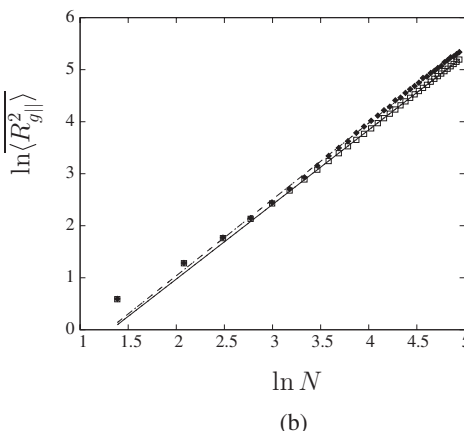
with scaling function $G_\perp(x) = \text{const}$ for $T > T_A$ and $G_\perp(x) = x^{-\frac{2\nu}{\phi_s}}$ for $T < T_A$.

The component of the gyration radius in direction parallel to the surface, $\langle R_{g||}^2 \rangle$, has similar scaling behavior: For $T > T_A$ the usual bulk behavior is reproduced, whereas for $T < T_A$ the polymer chain predominantly lies on the surface and behaves statistically as two-dimensional[6]

$$\langle R_{g||}^2 \rangle \sim \begin{cases} N^{2\nu}, & T > T_A, \\ N^{2\nu_2}(T_A - T)^{-\frac{2\nu_2 - \nu}{\phi_s}}, & T < T_A. \end{cases} \quad (13)$$

where ν_2 is the corresponding critical exponent in two dimensions ($\nu_2 = 3/4$ (Ref. [43]) in the homogeneous case). Again, this allows a scaling representation:

$$\langle R_{g||}^2 \rangle \sim N^{2\nu} G_{||}(|T - T_A|N^{\phi_s}), \quad (14)$$

with scaling function $G_{||}(x) = \text{const.}$ for $T > T_A$ and $G_{||}(x) = x^{\frac{2\nu_2 - \nu}{\phi_s}}$ for $T < T_A$.

Our results for $\overline{\langle R_{g\perp}^2 \rangle}$ as a function of temperature are presented in Fig. 3. At each temperature, the polymer layer thickness on the homogeneous surface is smaller than that on the percolation cluster due to stronger attraction to the surface. For $T < 0.5$, the layer thickness is so small that the conformations are basically two-dimensional in both cases. $\overline{\langle R_{g||}^2 \rangle}$ as function of temperature is shown in Fig. 4(a). Examining the N-dependence of the parallel component of the gyration radius at temperatures well below the adsorption point (Fig. 4(b)), we can find estimates of the critical exponent ν_2 by least-square fitting. For the case of a homogeneous surface, the value $\nu_2 = 0.742 \pm 0.006$ is restored. For the critical exponent, governing the scaling for a polymer chain adsorbed on an attractive percolation cluster, a value $\nu_2^{p_c} = 0.772 \pm 0.006$ is obtained. This exponent is compatible with the one for the average size of a polymer residing on the sites of a two-dimensional percolating cluster, $\nu_2^{p_c} = 0.782 \pm 0.003$.[44]

The study of size ratio $g \equiv \overline{\langle R_{g\perp}^2 \rangle}/\overline{\langle R_{g||}^2 \rangle}$ can be used to estimate the critical adsorption temperature. Remembering the scaling representations of the components of the gyration radius (12) and (14), one has

$$g = G_\perp(|T - T_A|N^{\phi_s})/G_{||}(|T - T_A|N^{\phi_s}) = G(|T - T_A|N^{\phi_s}). \quad (15)$$

At the adsorption critical point ($T \to T_A$), this ratio becomes independent of N and thus, when plotting g vs T for different N, all curves should intersect in a single point which namely gives T_A. In Fig. 5, we present our results for the size ratio in the cases of (a) a homogeneous attractive surface and (b) the fractal substrate. The range of positions of points of intersection enables us to obtain estimates of the adsorption transition critical temperature: $T_A = 3.5 \pm 0.1$, $T_A^{p_c} = 2.7 \pm 0.1$.
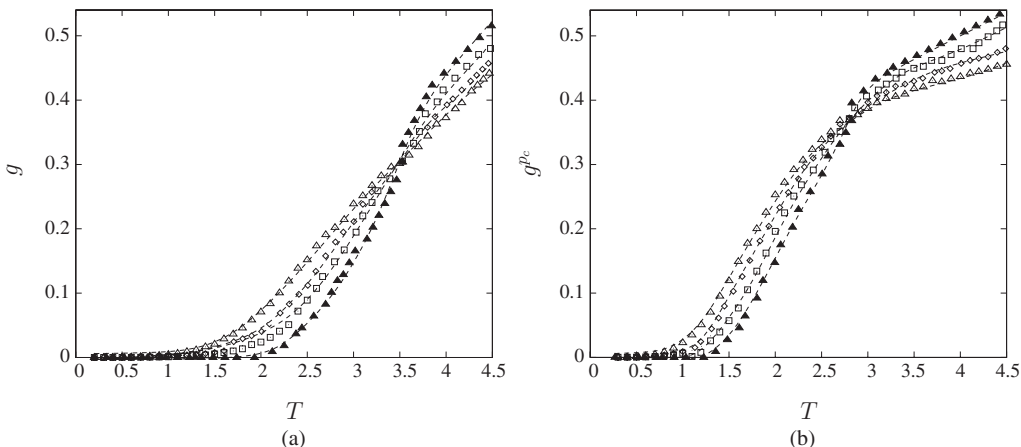

(a)

(b)

FIG. 4. Component of gyration radius of the polymer chain in direction parallel to the surface for the cases of a homogeneously attractive surface (squares) and an attractive percolation cluster (filled diamonds) as (a) a function of temperature and (b) as a function of N in double logarithmic scale at $T = 0.1$. Solid line: least-square fitting with $\nu_2 = 0.742 \pm 0.006$, dashed line: least-square fitting with $\nu_2^{p_c} = 0.772 \pm 0.006$.

FIG. 5. The size ratio $g = \overline{\langle R_{G\perp}^2 \rangle} / \overline{\langle R_{g\|}^2 \rangle}$ of the polymer chain near (a) a homogeneously attractive surface and (b) an attractive percolation cluster as a function of temperature. Triangles: $N = 80$, diamonds: $N = 100$, squares: $N = 120$, filled triangles: $N = 140$.

The characteristics of the adsorption transition can be obtained by examining the fluctuations of the adsorption energy near the transition point. The specific heat per monomer is given by

$$C = \frac{1}{NT^2}\left(\overline{\langle N_s^2 \rangle} - \overline{\langle N_s \rangle^2}\right). \qquad (16)$$

Taking into account Eq. (8), one obtains the scaling form for the specific heat[6]

$$C \sim N^{2\phi_s - 1} H(|T - T_A| N^{\phi_s}). \qquad (17)$$

The peak structure of C as a function of temperature indicates transitions or crossovers between physically different states. In the problem under consideration, this corresponds to the transition between bulk and adsorbed regimes. Figure 6 shows the typical specific-heat behavior of SAWs grafted to a homogeneous surface and percolation clusters, respectively.

Note, that the maximum of the specific heat per monomer grows with N for the case of a plain surface, whereas for the case of a fractal surface it decreases with increasing N. Assuming that the value of the specific heat at its maximum (the height of the specific-heat curve) $C_{\max}(N)$ at each N is already close enough to the asymptotic region where Eq. (17)

holds, we can estimate the crossover exponent ϕ_s by fitting the curves in Fig. 7(a) to the form

$$C_{\max}(N) \sim a + bN^{2\phi_s - 1}, \qquad (18)$$

where a and b are some constants. We obtain $\phi_s = 0.509 \pm 0.009$, $\phi_s^{p_c} = 0.425 \pm 0.009$.

For finite chain length N, the temperature defined by the position of the specific-heat maximum $T_{\max}(N)$ is well below the transition temperature T_A of an infinitely long polymer macromolecule. This finite-size deviation obeys the scaling behavior

$$T_{\max}(N) - T_A \sim N^{-\phi_s}. \qquad (19)$$

Fitting the curves in Fig. 7(b) to this form, and making use of the estimates for ϕ_s found by us, we receive for the critical temperature of the adsorption transition onto a homogeneous surface $T_A = 3.47 \pm 0.02$, and for the case of a percolation cluster the result of fitting gives $T_A^{p_c} = 2.64 \pm 0.02$.

The values obtained could be verified by plotting, e.g., the scaling function of the order parameter (8) as a function of its argument in double logarithmic scale for different chain lengths N (Fig. 8). As expected, a data collapse is obtained. The "upper" branches in both plots correspond to $T < T_A$ and
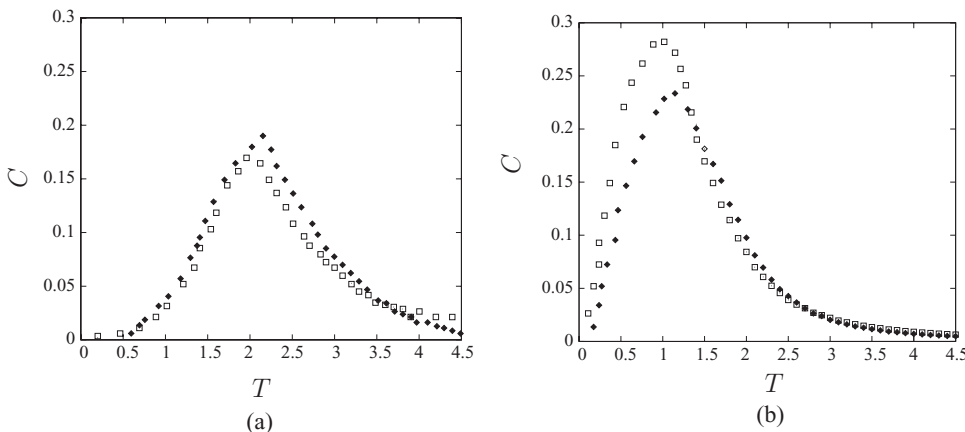

FIG. 6. Specific heat per monomer as a function of temperature for a polymer chain near (a) a homogeneously attractive surface and (b) an attractive percolation cluster as a function of temperature. Squares: $N = 40$, filled diamonds: $N = 100$.
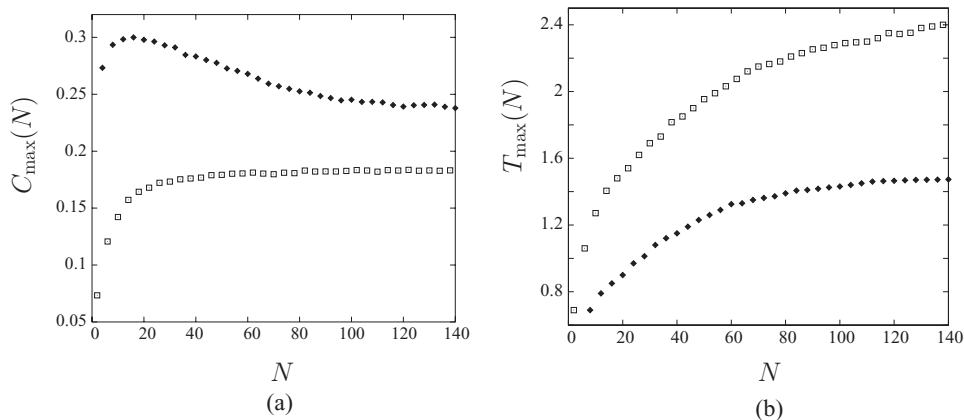
FIG. 7. (a) The maximum heights of the specific-heat curves and (b) the temperatures defined by the position of the specific-heat maximum for a polymer chain near a homogeneously attractive surface (squares) and an attractive percolation cluster (filled diamonds) as functions of N.

scale with their argument as $x^{(1-\phi_s)/\phi_s}$, according to Eq. (9). The "lower" branches corresponding to $T > T_A$, after reaching the asymptotic limit, should decrease according to Eq. (9) as x^{-1}.

Finally, we analyze the shape of a typical spatial conformation, which attains a polymer chain in the adsorbed state. The measure of the shape properties of a polymer chain in d dimensions can be characterized[45, 46] in terms of the gyration tensor $\mathbf{Q}$ with components

$$Q_{ij} = \frac{1}{2N^2} \sum_{n=1}^{N} \sum_{m=1}^{N} \left(x_n^i - x_m^i\right)\left(x_n^j - x_m^j\right), \quad i, j = 1, \ldots, d, \tag{20}$$

where x_n^i are the components of the position vector $\vec{R}_n$. Special cases are the squared radius of gyration parallel and perpendicular to the surface in Eq. (10), $R_{g\parallel}^2 = Q_{11} + Q_{22}$ and $R_{g\perp}^2 = Q_{33}$. In general, the spread in eigenvalues λ_i of the gyration tensor describes the distribution of monomers inside the polymer coil and thus measures the asymmetry of a molecule; in particular, for a symmetric (spherical) configuration all the

eigenvalues λ_i are equal, whereas for completely stretched, rod-like configurations all eigenvalues are zero except of one. To compute the quantities λ_i analytically is, however, difficult, because one must explicitly diagonalize the gyration tensor for each realization in an ensemble of polymers. It was thus proposed[46, 47] to characterize the asymmetry of polymer configurations by rotationally invariant universal quantities, such as the asphericity A_d, defined as

$$A_d = \frac{1}{d(d-1)} \sum_{i=1}^{d} \frac{(\lambda_i - \bar{\lambda})^2}{\bar{\lambda}^2} = \frac{d}{d-1} \frac{\text{Tr}\,\hat{\mathbf{Q}}^2}{(\text{Tr}\,\mathbf{Q})^2}, \tag{21}$$

with $\bar{\lambda} = (1/d) \sum_{i=1}^{d} \lambda_i$ and $\hat{\mathbf{Q}} \equiv \mathbf{Q} - \bar{\lambda}\,\mathbf{I}$ (here $\mathbf{I}$ is the unity matrix). This universal quantity equals zero for a spherical configuration and takes a maximum value of one in the case of a rod-like configuration. Thus, the inequality $0 \leq A_d \leq 1$ holds. Numerous studies indicate that a typical flexible polymer chain in good (bulk) solvent takes on the shape of an elongated ellipsoid with $\langle A_2 \rangle = 0.501 \pm 0.003$,[48] $\langle A_3 \rangle = 0.431 \pm 0.002$.[49]
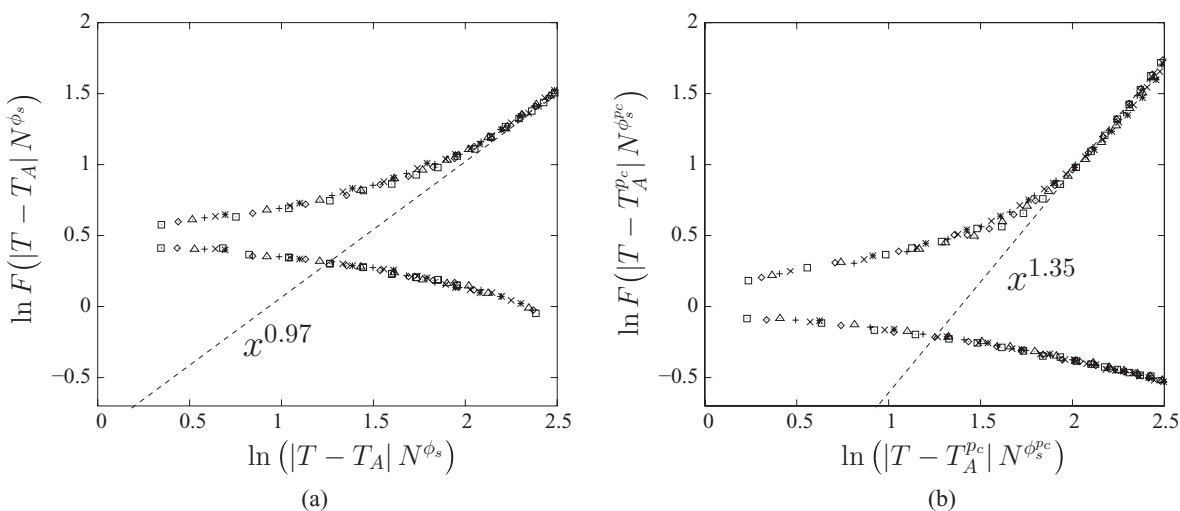

FIG. 8. The scaling function (8) as a function of its argument for a polymer chain near (a) a homogeneously attractive surface and (b) an attractive percolation cluster. Dashed lines are results of fitting to the scaling form (9) for $T < T_A$. Squares: $N = 40$, diamonds: $N = 60$, triangles: $N = 80$, pluses: $N = 100$, crosses: $N = 120$, stars: $N = 140$.

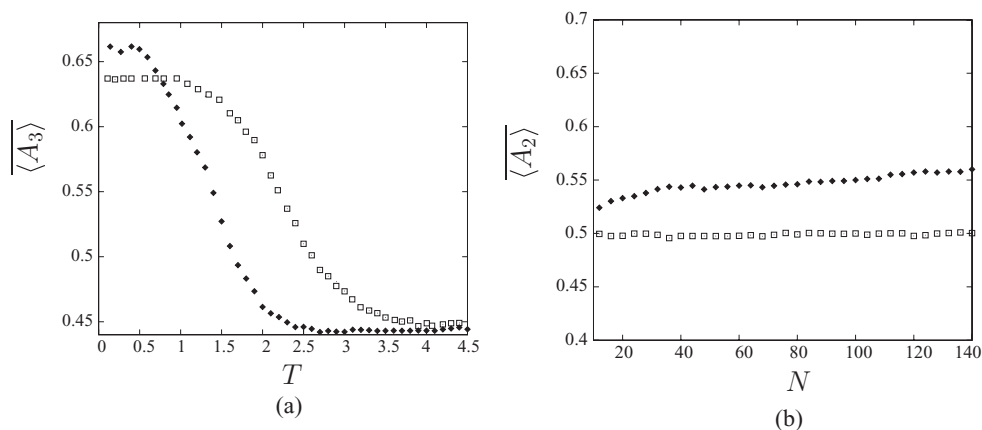FIG. 9. (a) Averaged three-dimensional asphericity $\overline{\langle A_3 \rangle}$ of a polymer chain near a homogeneously attractive surface (squares) and an attractive percolation cluster (filled diamonds) as a function of temperature and (b) the two-dimensional analog $\overline{\langle A_2 \rangle}$ as a function of N at $T = 0.1 \ll T_A$ deep in the adsorbed phase.

Our results for the averaged asphericity of a polymer grafted to a surface as a function of temperature are given in Fig. 9(a). In the high-temperature regime, both curves tend to the bulk value of $\langle A_3 \rangle$, whereas as temperature decreases, the anisotropy of polymer configuration grows. Note, however, the principal point. When the temperature is well above the adsorption transition, the polymer coil in bulk is a three-dimensional object and thus is characterized by the quantity $\langle A_3 \rangle$. However, in the adsorbed state (well below T_A), the polymer lies on the surface and can be treated rather like a two-dimensional object, thus $\langle A_2 \rangle$ is the more natural characteristic. The quantity A_2 of a two-dimensional object can, however, be simply related to A_3, evaluating Eq. (21), e.g., at $\lambda_3 = 0$ with arbitrary λ_1, λ_2:

$$A_3 = \frac{1}{4} + \frac{3}{4} A_2. \tag{22}$$

Definition (21) is an *extrinsic* measure for the asphericity, depending on the dimension of the embedding space. Of course, in the present situation, it would be nicer to come up with an *intrinsic* measure, similar to Gauss' curvature definition. The asphericity $\overline{\langle A_2 \rangle}$ of a polymer adsorbed on a homogeneously attractive surface and attractive percolation cluster is given in Fig. 9(b) as a function of N. For finite chain length N, the values of $\overline{\langle A_2(N) \rangle}$ differ from those for infinitely long chains. This finite-size deviation obeys scaling behavior with N,

$$\overline{\langle A_d(N) \rangle} = \langle A_d \rangle + b_1 N^{-\Delta}, \tag{23}$$

where b_1 is a constant and Δ is the correction-to-scaling exponent: $\Delta(d = 2) = 1.5$ (Ref. 50) in the homogeneous case. The shape parameter estimates can be obtained by least-square fitting of Eq. (23). For the case of the pure lattice, we receive $\langle A_2 \rangle = 0.502 \pm 0.006$, whereas for the polymer on the attractive percolation cluster, we have $\overline{\langle A_2^{p_c} \rangle} = 0.567 \pm 0.006$, which within error bars agrees with the corresponding value found by us previously by analyzing the conformational statistics of polymers on underlying percolation clusters.[51] Note, that the corresponding values of the three-dimensional asphericity according to Eq. (22) are: $\langle A_3 \rangle = 0.627 \pm 0.006$, $\overline{\langle A_3^{p_c} \rangle} = 0.675 \pm 0.006$, which agree with the $T \rightarrow 0$ limit in Fig. 9(a). The principal qualitative con-

clusion from these shape parameters is that typical conformations of a polymer chain, which is adsorbed on an attractive percolation cluster, are more anisotropic than those for a homogeneously attractive surface due to the complicated fractal structure of the adsorbing "sieve."

IV. CONCLUSIONS

We have studied the adsorption of flexible polymer macromolecules on an attractive percolation cluster, formed on a regular two-dimensional disordered lattice at critical concentration p_c of occupied sites. We treat such disordered surface as the $z = 0$ plane of a regular simple-cubic three-dimensional lattice. In our model, the sites which do not belong to the percolation cluster, are penetrable for the polymer chain. The percolation cluster is a fractal object, characterized by the fractal dimension $d_s^{p_c} = 91/49 \simeq 1.89$,[37] thus we have the problem of polymer adsorption on a fractal substrate.

The conformational properties of polymer chains grafted to a percolation cluster are studied with the PERM.[40] Examining the peak structure of the heat capacity, we find an estimate for the surface crossover exponent, governing the scaling of the adsorption energy in the vicinity of the transition point, $\phi_s^{p_c} = 0.425 \pm 0.009$, and for the adsorption transition temperature, we obtain $T_A^{p_c} = 2.64 \pm 0.02$. As expected, the adsorption is diminished, when the fractal dimension of the surface is smaller than that of the plain Euclidean surface due to the smaller number of contacts of monomers with attractive sites.

We also analyzed the shape of typical spatial conformations that a polymer chain attains in the adsorbed state. The asymmetry of the shape can be characterized by rotationally invariant universal quantities, such as the asphericity A_d, which equals zero for a spherical configuration, and takes on a maximum value of one in the case of a completely stretched rod-like configuration. For the polymer on the attractive percolation cluster we received the value $\overline{\langle A_2^{p_c} \rangle} = 0.567 \pm 0.006$, which is larger than that on the plain surface, $\langle A_2 \rangle = 0.502 \pm 0.006$. The principal qualitative conclusion from our analysis of the shape parameters is that typical conformations of a polymer chain that is adsorbed on an attractive "sieve" formed

by a percolation cluster are more anisotropic than those of a homogeneously attractive surface.

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